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Leaching of Methyl Isothiocyanate in Plainfield Sand Chemigated with Metam-Sodium

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Abstract: Soil column studies were undertaken to investigate the influence of soil water content and irrigation on leaching, distribution and persistence of methyl isothiocyanate (MITC) in a sandy soil chemigated with the soil fumigant metam-sodium. No leaching was obtained from columns at low water content (0·042 or 0·074 cm^3 cm^{-3}). However, 8·4 (±2·8), 34·2 (±7·4) and 119·4 (±8·3) μg of MITC leached from columns at 0·105, 0·137 and 0·168 cm^3 cm^{-3} water content, respectively. Increased leaching resulted from sprinkler application of 25-mm of water to columns at 0·137 cm^3 cm^{-3} water content. Leaching of MITC constituted only a small fraction of the amount applied even in the worst case. Methyl isothiocyanate persisted in soil for 15 days at 2°C in varying amounts under the different water regimes. Relatively high amounts of MITC residues (8–12 mg kg^{-1} soil) were detected in the top 25-cm layer of all the soil columns. Degradation was the major pathway of dissipation for the chemical despite the soil water regime.

Key words: fumigant, percolation, chemigation.

1 INTRODUCTION

Recently, concern over environmental quality has increased public awareness of ground water contamination with pesticides. Potential health hazards of pesticides found in potable ground waters[1–3] have raised questions concerning the possibility of similar environmental consequences from the use of other agrochemicals. Methyl isothiocyanate (MITC), the active conversion product of the soil fumigant metam-sodium (sodium *N*-methyldithiocarbamate), is a possible suspect for contaminating ground water. This is due to its high leaching characteristics and increased use in the state of Wisconsin at locations overlying shallow water tables.[4]

Leaching depends on the chemical characteristics of the pesticide, environmental conditions, and the method, time, formulation and amount of pesticide applied.[5] High water solubility and low soil sorption coefficients strongly influence the tendency of a pesticide to leach. Metam-sodium and MITC are both relatively soluble in water[6] and are weakly retained by soils with moderate amounts of orgnic matter.[7,8]

Several soil variables affect the efficacy of metam-sodium and its fate in the soil, and influence the likelihood of MITC leaching into ground water. Important variables include soil water content before treatment, soil temperature (and thus timing of application), water used during application, soil texture, and amount of irrigation water and/or rainfall after application. Some farmers in the region irrigate their fields after metam-sodium application, trying to reduce irritant releases of MITC vapors from the soil. However, this practice may enhance the potential for MITC leaching beyond the zone of optimum efficacy and perhaps even to ground water.

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The objective of this study was to determine the fate of MITC when metam-sodium was applied with irrigation water to soil columns under different soil water conditions, with particular emphasis on MITC leaching, and its distribution and persistence in soil.

2 EXPERIMENTAL METHODS

2.1 Column preparation and experimental setup

A temperature-controlled growth room in the University of Wisconsin-Madison's Biotron was used to run two soil column experiments. A set of nine columns was made from 91·5 cm × 20·3 cm ID Schedule 40 PVC pipes. The inner walls of columns were lined with 0·79-mm Teflon sheets to prevent sorption of lipophilic chemicals to PVC surfaces. The soil used to pack the columns was non-sterile Plainfield sand (mixed, mesic Typic Udipsamment). The soil was taken from a single site in a field at the University of Wisconsin-Madison Experiment Station near Hancock, WI. Table 1 shows some of the characteristics of the soil used.

The field soil profile was divided into three layers and the soil from each layer was collected separately. Columns were packed in the same horizonation and bulk densities of soil profiles found in the field. A bulk density of 1·40 g cm^{-3} was used for the upper third of the profile and 1·65 g cm^{-3} for the lower two layers. The column was packed by adding a 5-cm layer of soil at a time.

Columns were arranged in two rows and allowed to hang freely from a rack. Columns were fitted at the bottom with 1-bar fritted ceramic plates (Soilmoisture, Santa Barbara, CA) and Teflon-lined aluminum funnels to connect a vacuum system to withdraw leachate into collection bottles. The vacuum system was operated continuously under a suction of − 0·33 bar to simulate the free drainage of the Plainfield soil *in situ*.[9,10]

A short piece of a PVC cylinder was fastened to the top of each column and the joint was tightly sealed using a clear silicone-rubber sealant (Dow Corning Inc., Midland, MI, USA). The lid of the top chamber was fitted with an irrigator. The irrigator system consisted of a reservoir, connecting tube lines, stopcocks, delivery tubes and syringe needles. The delivery tube, 79-mm ID Tygon tubing about 270 cm long, was coiled and fixed on the lid. Holes were made on the lid to accommodate twenty-eight 20-gauge 2·5 cm long syringe needles. These were attached by the sharp end to the coiled delivery tube while the needle hubs were inside the chamber. These needles were arranged so that they formed evenly spread rows inside the chamber to allow even spreading of the fumigant and/or water. Silicone-rubber sealant was used to form an airtight irrigation system. The columns were essentially a closed system that did not allow MITC volatilization. Samples of the atmosphere in the irrigation chamber were taken by drawing 0·9 ml min^{-1} of air through an ethyl acetate trap.

The Biotron growth room was used to establish the temperature regime for the experiments. The chosen temperature (2°C) reflects application under typically cold Wisconsin conditions (late fall or early spring chemigation). In the first experiment three soil water levels, 0·042, 0·105 and 0·168 cm^3 cm^{-3} were employed. In the second experiment the treatments were 0·074, and 0·137 cm^3 cm^{-3}, and a third treatment of 0·137 cm^3 cm^{-3} followed by irrigation 24 and 48 h after application of the fumigant. The initial water contents were established by adding water to each 5-cm layer of soil during packing. In the treatment with additional irrigation, 12·5 mm was added at both 24 and 48 h following chemigation. Each treatment was replicated three times. Each experiment was run for 15 days. Drainage water was collected from the bottom of columns and assayed for MIT.

2.2 Fumigant application

Solutions of metam-sodium 345 g kg^{-1} SP (Busan 1020; Buckman Laboratories, Memphis, TN, USA) were applied to the columns at a rate of 480 litre ha^{-1}.

TABLE 1
Selected Physical and Chemical Characteristics of the Plainfield Sand Used

	Soil separates						
Soil depth (cm)	*Sand (%)*	*Silt (%)*	*Clay (%)*	*Organic matter (%)*	*Bulk density (g cm^{-3})*	*Field capacity (cm^3 cm^{-3})*	*Calcium carbonate (%)*
0–30	88·5	7·5	4·0	0·41	1·40	0·210	0·42
30–60	95·3	3·4	1·3	0·16	1·65	0·132	0·37
60–90	98·1	1·5	0·4	0·18	1·65	0·132	0·40

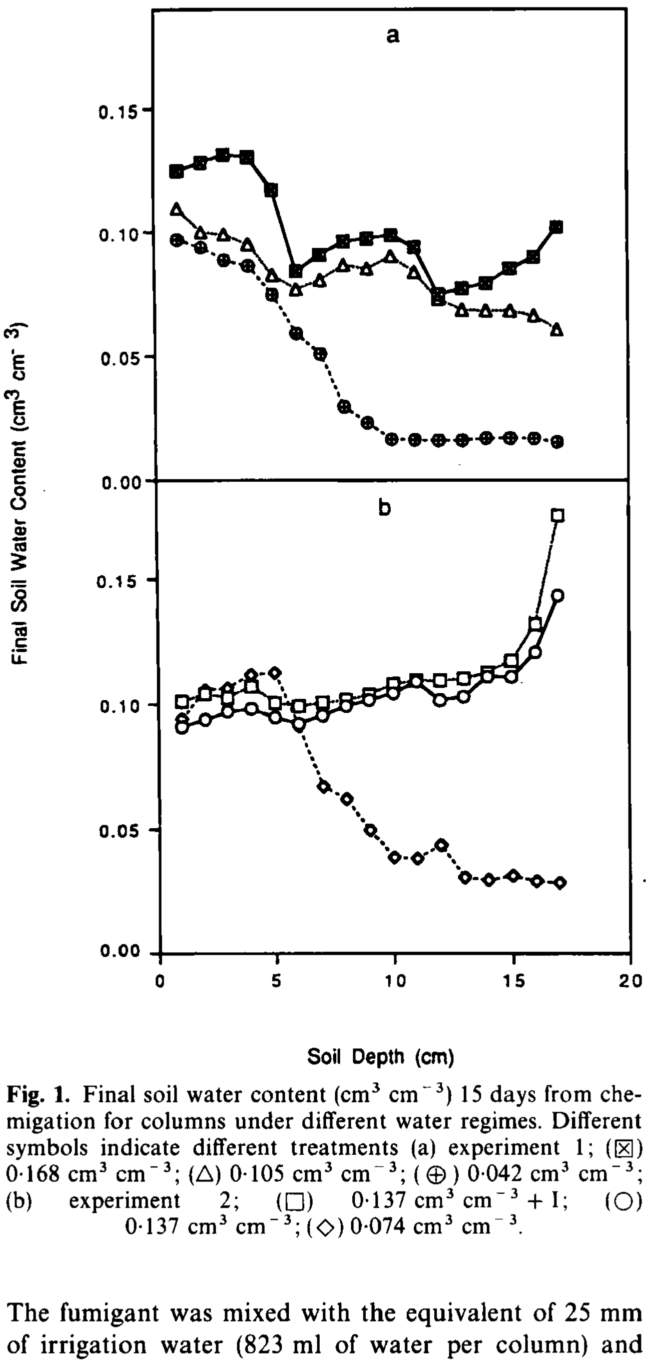

Fig. 1. Final soil water content ($cm^3\ cm^{-3}$) 15 days from chemigation for columns under different water regimes. Different symbols indicate different treatments (a) experiment 1; (⊠) 0·168 $cm^3\ cm^{-3}$; (△) 0·105 $cm^3\ cm^{-3}$; (⊕) 0·042 $cm^3\ cm^{-3}$; (b) experiment 2; (□) 0·137 $cm^3\ cm^{-3}$ + I; (○) 0·137 $cm^3\ cm^{-3}$; (◇) 0·074 $cm^3\ cm^{-3}$.

The fumigant was mixed with the equivalent of 25 mm of irrigation water (823 ml of water per column) and applied evenly by the irrigator across the soil surface. The initial water content and distribution within columns was altered by the water added through the chemigation and/or irrigation. Final soil water contents and distribution for both experiments are presented in Fig. 1.

The concentration of metam-sodium in the application water was equivalent to 619 mg $litre^{-1}$. The theoretical concentration of MITC was equivalent to 520 mg $litre^{-1}$ assuming 84% conversion of metam-sodium to MITC. This value is the mid-point of the range (78–90%) in the literature for the conversion of metam-sodium to MITC.[11,12] Thus, the theoretical amount of MITC applied per column was 428 mg.

TABLE 2
Accuracy and Precision Data for MITC Extraction

Medium	*MITC added* ($\mu g\ litre^{-1}$)	*Number of samples*	*Average recovery* (%)($\pm SD$)
Water	0·02	10	88 (±3)
Water	0·20	15	90 (±3)
Soil	0·02	10	85 (±4)
Soil	0·20	15	100 (±5)

2.3 Sampling and analytical methods

The leachate was collected frequently in the first few days of the experiment. The collection interval was lengthened after that to allow enough water to drain to facilitate the extraction of the chemical. At the end of each 15-day run the soil was removed from the columns in 5-cm layers and subsamples were taken to measure the concentration of MITC residue remaining in the soil and the final soil water content.

Methyl isothiocyanate in the leachate was extracted by the solvent-flush technique described in the Manual of the Wisconsin State Laboratory of Hygiene.[13] A 500-ml sample was transferred to 2-litre separatory funnel and 100 g muffle-furnace dried sodium chloride dissolved in the sample. Each sample was extracted twice with 10-ml aliquots of methylene chloride. The extract was percolated through a drying tube containing a small amount of muffle-furnace dried sodium sulfate and then transferred into a 15-ml centrifuge tube.

The extracted sample was analyzed using a Hewlett-Packard 5880A GC equipped with a nitrogen-phosphorus detector. The column used was a 1·8 m × 6 mm ID glass column packed with 4% SE-30/6% OV-210. Nitrogen (99·99% pure) was used as a carrier gas at 30 ml min^{-1}. The temperatures used were: 90°C for the column oven, 260°C for the injector and 275°C for the detector.

Extraction of MITC residues from soil was accomplished by a method described by Leistra *et al.*[12] Soil samples were collected in 200-ml glass jars that were immediately closed with gas-tight screw-caps. The content of each jar was mixed by shaking by hand and the jar kept frozen at −12°C until the time of extraction. Samples of about 50 g of soil were quickly weighed into 200-ml glass jars containing 24 ml ethyl acetate and 25 ml water. The jars were sealed with screw-caps and mechanically shaken for 2 h. The ethyl acetate layer was separated by centrifugation at 2000 rev min^{-1} for 2 min. The solutions in ethyl acetate were diluted if necessary and MITC concentrations were measured using the GC.

The above two methods were tested for recovery by running tests on spiked samples of soil and water. Results of these tests are given in Table 2. Data were corrected for recovery according to the results of these tests.

2.4 Experimental design and data analysis

A set of nine soil columns (experimental units) was used in each of these experiments. A completely randomized design (CRD) with three replicates was used for the analysis of data. Data were analyzed with the analysis of variance (ANOVA), and mean separations were achieved by calculating least square differences (LSD) between water treatment means using SAS.[14] A non-parametric statistical analysis was performed on the data using SAS[14] because some treatment means had values of zero making parametric statistical analysis inappropriate. The Kruskal-Wallis test was performed on the data and χ-squared approximation was used to test the null hypothesis H° of no difference between treatment means.

3 RESULTS

3.1 Water drainage and MITC leaching

No drainage was obtained from columns at 0·042 or 0·074 cm^3 cm^{-3} water content (Fig. 2). Drainage volumes of 151 ($\pm$47), 231 ($\pm$10) and 815 ($\pm$78) ml per column were obtained for columns equilibrated at 0·105, 0·137 and 0·168 cm^3 cm^{-3}. However, a higher

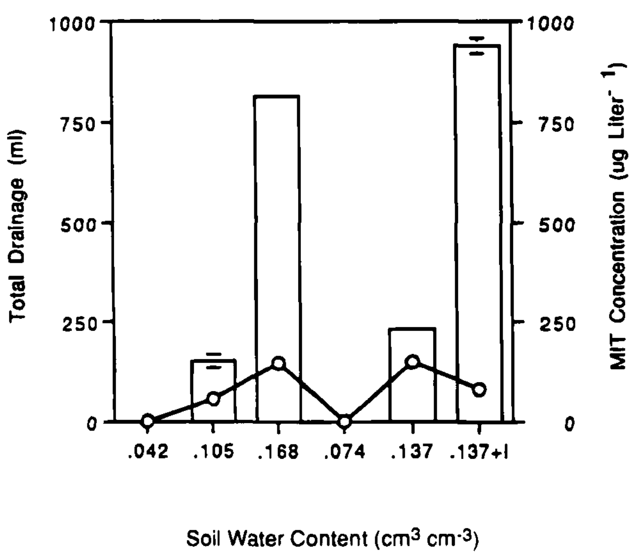

Fig. 2. Average total drainage per column (ml) (bars) and MITC concentration in leachate (μg litre^{-1}) (curve) at different water contents. Error bars are $\pm$S.E.; n = 3.

volume of 939 ($\pm$7) was obtained for columns initially at 0·137 cm^3 cm^{-3} and supplied with 25 mm of irrigation.

In the first experiment, total leachate loss per column (μg) was higher at 0·168 cm^3 cm^{-3} ($P = 0{\cdot}01$) when compared to the other water regimes (Table 3). Without post-application irrigation only 34·2 μg of MITC was collected at 0·137 cm^3 cm^{-3}. However, significantly higher ($P = 0{\cdot}01$) MITC leachate loss resulted when chemigation was followed by 25 mm of irrigation water in the second experiment.

Highest MITC concentrations in leachate were obtained from wet soil (0·168 and 0·135 cm^3 cm^{-3}) in both experiments. However, following chemigation by irrigation resulted in lower MITC leachate concentration (Fig. 2).

3.2 Distribution of MITC residues in soil

Fifteen days after chemigation MITC residue was detected in soil regardless of water content. Generally, relatively high amounts of MITC residues were detected in the top 25-cm layer in both experiments (Fig 3(a)(b)). In drier soil (0·042 and 0·074 cm^3 cm^{-3}) MITC residue concentrations were highest in the top soil layer with little or no residue in the lower layers. At medium water levels (0·105 and 0·137 cm^3 cm^{-3}) MITC residue was present in all layers but in higher concentrations in the middle layer compared to the other two regimes. At 0·137 cm^3 cm^{-3}, when metam-sodium application was followed by irrigation, MITC was leached to the bottom of the column, resulting in high residue in that layer. At 0·168 cm^3 cm^{-3} MITC residue concentrations were low throughout the column compared to the intermediate water levels.

In both experiments, the intermediate water levels (0·105 and 0·137 cm^3 cm^{-3}) resulted in the highest

TABLE 3
Results of ANOVA and Kruskal-Wallis Test (χ-squared Approximation) for MITC Leachate Loss per Column (μg) at the Various Soil Water Regimes

Water content (cm^3 cm^{-2})	*Leaching (μg)*	*F Value ($P = 0{\cdot}01$)*	*Sum of scores*[a]	*χ-squared ($P = 0{\cdot}02$)*
0·168	119·4	90·0[c]	24·0	7·4
0·105	8·4		15·0	
0·042	0·0		6·0	
0·137 + I[b]	74·9	668·5[c]	24·0	7·4
0·137	34·2		15·0	
0·074	0·0		6·0	

[a] Sum of scores expected under H° is 15·0.
[b] I is 12·5-mm irrigation applied at 24 and 48 h after chemigation.
[c] Means are significantly different from each other by F-test ($P = 0{\cdot}01$).

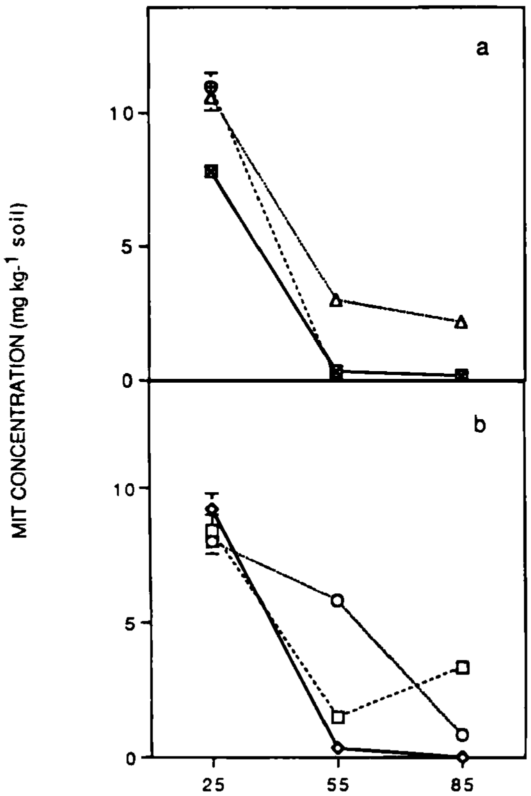

Fig. 3. Concentration of MITC residue in soil (mg kg^{-1}) after 15 days from chemigation at 2°C and different soil water conditions. Different symbols indicate different treatments (a) experiment 1; (☒) 0·168 cm^3 cm^{-3}; (△) 0·105 cm^3 cm^{-3}; (⊕) 0·042 cm^3 cm^{-3}; (b) experiment 2; (□) 0·137 cm^3 cm^{-3} + I, (○) 0·137 cm^3 cm^{-3}; (◇) 0·074 cm^3 cm^{-3}. Error bars are ±S.E.; n = 3.

amounts of MITC residue left in the soil in comparison to the other two regimes (Table 4).

3.3 MITC mass balance

Since MITC volatilization into the sealed chamber never exceeded 60 μg (0·01% of the amount applied), the amount of MITC degraded in soil was calculated as the theoretical amount applied per column (428 mg) minus the amounts leached and remaining as residue in soil (Table 4). Degradation clearly constitutes the major pathway of dissipation for the chemical regardless of soil water content.

TABLE 4
Amounts of MITC (Mean (±S.E.)) Leached, Degraded and Remaining as Residue 15 Days after Chemigation at Various Soil Water Regimes

Treatment (*cm^3 cm^{-3}*)	*Leaching* (*μg*)	*Residue* (*mg*)	*Degradation* (*mg*)
0·168	119·4 (±8·3)	40·8 (±12·8)	387·1 (±13·4)
0·105	8·4 (±0·3)	76·4 (±12·2)	351·6 (±27·1)
0·042	0·0	55·1 (±6·7)	372·9 (±12·1)
0·137 + I	74·9 (±2·8)	132·9 (±4·2)	295·0 (±11·1)
0·137	34·2 (±7·4)	199·7 (±10·7)	228·3 (±10·4)
0·074	0·0	116·6 (±4·5)	311·4 (±5·6)

4 DISCUSSION

Most researchers agree that gases move through soil mainly by diffusion and not in solution by mass flow of water. With water-soluble compounds, such as metam-sodium, whose activity depends on a volatile, yet water-soluble, breakdown product, gas diffusion is less important than water flow.[6,12] Generally, soil water affects water-insoluble gas diffusion greatly because of the physical blockage of free pore space by water.[15] Results obtained in this study for the influence of soil water content on MITC movement can be explained on the same grounds. In a nearly saturated soil (0·168 cm^3 cm^{-3}), MITC leached through a 90-cm soil column relatively easily. However, at 0·137 cm^3 cm^{-3} a smaller volume of drainage water containing MITC penetrated through the columns. No leaching occurred through columns containing dry soils. Thus, penetration of MITC by vapor was less than by water and the higher the soil water content the higher the leaching of MITC. Furthermore, irrigation (25 mm of water) following chemigation at 0·137 cm^3 cm^{-3} water content resulted in increased MITC leaching.

Our earlier studies demonstrated that soil temperature influences MITC leaching and persistence in soil. Generally, the higher the temperature, the lower the leaching loss. At higher temperatures the loss of MITC through degradation is enhanced, leaving less to leach with percolating water.[7,16] In this study and under cold temperature, MITC persisted for two weeks in soils. These results support the findings of Smelt and Leistra[7] who concluded that the fumigant may persist for several months in cold soil.

Residues of MITC remaining in soil after 15 days following chemigation were highest in the top 25-cm of the soil profile and decreased with depth regardless of water content. This may be attributed to the fact that Plainfield sand contains higher organic matter in the A horizon than in the underlying layers. Such soils may present much more resistance to elution of dissolved MITC than pure sands, due to sorption of MITC on the organic fraction in this layer. Further flushing of the system led to more leaching as shown by the present study when chemigation was followed by irrigation.

It can be concluded from this study that a small amount of MITC may leach through the soil profile with percolating water under wet conditions or when irrigation follows chemigation in a less saturated soil. As was suggested by Jury *et al.*[17] mobility of a chemical

alone is not a good indicator of its ground water pollution potential, but rather a combination of mobility and persistence. Thus the potential for ground water contamination by MITC is low due to its low leaching and fast degradation.

Besides the risk of ground water contamination by MITC when leaching is allowed, satisfactory control of the soil-borne pathogens may also be jeopardized, since, for the chemical to be effective, adequate concentrations of active ingredient must persist long enough within the root zone. This was confirmed by our recent work on the efficacy of the fumigant against *Verticillium dahliae* Kleb.[16]

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REFERENCES

1. Chesters, G., Anderson, M. P., Shaw, B., Harkin, J. M., Meyer, M., Rothschild, E. & Manser, R., Aldicarb in ground water. *Report Water Resources Center*, University of Wisconsin-Madison. WI, USA, 1982, 38 pp.
2. Cohen, S. Z., List of potential ground water contaminants. *Office of Pesticides Program Report TS-769c*. Environmental Protection Agency, Washington DC, USA, 1984.
3. Holden, P. W., *Pesticides and ground water quality. Issues and problems in four states.* Board on Agriculture and Natural Resources Council, Washington DC, USA, 1986.
4. Neher, N. J., Setting Wisconsins groundwater standards. *Proc. Fertilizer, Aglime and Pest Management Conference*, Madison, WI, USA, 1987, pp. 238–41.
5. Chesters, G., Simsiman, G. V., Levy, J. L., Alhajjar, B. J., Fathulla, R. N. & Harkin, J. M., Environmental fate of Alachlor and metolachlor. *Rev. Environ. Contam. Toxicol.*, **110** (1989) 1–74.
6. Adams, P. B., Soil fumigation by chemigation with metam. In *Methods of Evaluating Pesticides for Control of Plant Pathogens*, ed. K. Hickey. American Phytopathological Society, St. Paul MN, 1986, pp. 270–2.
7. Smelt, J. H. & Leistra, M., Conversion of metam-sodium to methyl isothiocyanate and basic data on the behavior of MIT in soil. *Pestic. Sci.*, **5** (1974) 401–7.
8. Gerstl, Z., Mingelgrin, U. & Yaron, B., Behavior of Vapam and MIT in soils. *Soil Sci. Soc. Proc.*, **41** (1977) 545–8.
9. Merrill, S. D., Raats, P. A. C. & Dirksen, P., Laterally confined flow from a point source at the surface of an inhomogeneous soil column. *Soil Sci. Soc. Am., J.*, **42** (1978) 851–7.
10. Roberts, J. A., Daniels, W. L., Bell, J. C. & Burger, J. A., Early stages of mine soil genesis in southwest Virginia. *Soil Sci. Soc. Am. J.*, **52** (1988) 716–23.
11. Gray, R. A., Rate of Vapam decomposition in different soils and other media. *Phytopathol.*, **52** (1962) 734.
12. Leistra, M., Smelt, J. M. & Nollen, H. M., Concentration relations for methyl isothiocyanate in soil after injection of metam-sodium. *Pestic. Sci.*, **5** (1974) 409–17.
13. Wisconsin State Laboratory of Hygiene, *Vapam, Manual of Chemical Analysis.* Madison, Wisconsin, USA, 1984.
14. SAS Institute, GLM Procedure. *SAS User's Guide: Statistics.* SAS Institute, Cary NC, 1985.
15. Munnecke, D. E., Fungicides in the soil environment. In *Fungicides*, ed. I. D. Tugerson. Academic Press, New York, 1967, pp. 509–59.
16. Saeed, I. A. M., Fate of metam-sodium in an irrigated loamy sand. Ph.D Thesis, University of Wisconsin, Madison, 1990, 146 pp.
17. Jury, W. A., Farmer, W. J. & Spencer, W. F., Behavior assessment model for trace organics in soil. *Environ. Qual.*, **13** (1984) 567–572.